

- 17 -

1999DE119

Patent Claims

1. A process for the preparation of alkylphosphonous
5 acid esters, which comprises
 - a) reacting elemental yellow phosphorus with alkylat-
ing agents in the presence of a base to give a
mixture which comprises, as principal constituents,
the (metal) salts of alkylphosphonous, phosphorous
10 and hypophosphorous acids,
 - b) esterifying the principal constituents of the
mixture from a) to give an ester mixture,
 - c) isolating the ester of the alkylphosphonous acid
from the ester mixture.
- 15 2. A process as claimed in claim 1, wherein the
alkylating agents are alkyl halides, dialkyl
sulfates, trialkyl phosphates, dialkyl carbonates
and/or formic acid ortho-esters.
3. A process as claimed in claim 1 or 2, wherein the
20 alkylating agent employed is methyl chloride,
methyl bromide and/or dimethyl sulfate.
4. A process as claimed in one or more of claims 1 to
3, wherein the bases are hydroxides, carbonates,
bicarbonates, amides, alkoxides and/or amine bases.
- 25 5. A process as claimed in one or more of claims 1 to
3, wherein the reaction in step a) is carried out
in a two-phase system comprising aqueous alkali or

- 18 -

alkaline-earth metal hydroxide or mixtures thereof and an organic solvent.

6. A process as claimed in one or more of claims 1 to 5, wherein the organic solvents employed are straight-chain or branched alkanes, alkyl-substituted aromatic solvents, water-immiscible or only partially water-miscible alcohols or ethers, alone or in combination with one another.
7. A process as claimed in one or more of claims 1 to 6, wherein the organic solvent employed is toluene, alone or in combination with alcohols.
8. A process as claimed in one or more of claims 1 to 7, wherein the reaction is carried out in the presence of a phase-transfer catalyst.
9. A process as claimed in claim 8, wherein the phase-transfer catalyst is a tetraalkylphosphonium halide, triphenylalkylphosphonium halide or tetraorganylammonium halide.
10. A process as claimed in one or more of claims 1 to 9, wherein the temperature during the reaction with the yellow phosphorus is from -20 to +80°C.
11. A process as claimed in one or more of claims 1 to 10, wherein the temperature during the reaction with the yellow phosphorus is from 0 to 30°C.

- 19 -

12. A process as claimed in one or more of claims 1 to 11, wherein the reaction is carried out under a pressure of from 0 to 10 bar.
13. A process as claimed in one or more of claims 1 to 5 12, wherein the principal constituents of the mixture from a) are esterified in step b) using a linear or branched alcohol of the general formula R-OH, where R is a linear or branched alkyl radical having 1 to 10 carbon atoms.
- 10 14. A process as claimed in one or more of claims 1 to 12, wherein the principal constituents of the mixture from a) are reacted with mineral acids to give a mixture of alkylphosphonous, phosphorous and hypophosphorous acids and at the same time the 15 (metal) salts of the mineral acids are precipitated, and the mixture of these acids is subsequently esterified.
15. A process as claimed in one or more of claims 1 to 14, wherein the water formed during the esterifica- 20 tion is removed by azeotropic distillation.
16. A process as claimed in one or more of claims 1 to 15, wherein the alcohol is n- or i-butanol, n-hexanol, ethylhexanol and/or amyl alcohol.
17. A process as claimed in one or more of claims 1 to 25 16, wherein the mineral acid is hydrochloric acid, sulfuric acid and/or phosphoric acid.

- 20 -

18. A process as claimed in one or more of claims 1 to 17, wherein the mineral acid is hydrochloric acid.
19. A process as claimed in one or more of claims 1 to 18, wherein the phosphines formed in small amounts in step a) are removed by oxidation.
20. A process as claimed in one or more of claims 1 to 19, wherein hydrogen peroxide is employed for the oxidation.
21. A process as claimed in one or more of claims 1 to 20, wherein the ester of the alkylphosphonous acid is removed by distillation in step c).
22. A process as claimed in one or more of claims 1 to 21, wherein the ester of the alkylphosphonous acid is n-butyl methylphosphonite, isobutyl methylphosphonite, n-hexyl methylphosphonite, 2-ethylhexyl methylphosphonite and/or amyl methylphosphonite.
23. The use of an alkylphosphonous acid ester prepared by a process as claimed in claims 1 to 22 for the preparation of organophosphorus compounds and derivatives.
24. The use of an alkylphosphonous acid ester prepared by a process as claimed in claims 1 to 22 as a precursor for chemical synthesis.
25. The use of an alkylphosphonous acid ester prepared by a process as claimed in claims 1 to 22 for the

- 21 -

preparation of phosphinic acids as starting materials for crop protection agents.

26. The use of an alkylphosphonous acid ester prepared by a process as claimed in claims 1 to 22 for the
5 preparation of flame retardants.

27. The use of an alkylphosphonous acid ester prepared by a process as claimed in claims 1 to 22 for the preparation of flame retardants for thermoplastic polymers, such as polyethylene terephthalate,
10 polybutylene terephthalate or polyamide.

28. The use of an alkylphosphonous acid ester prepared by a process as claimed in claims 1 to 22 for the preparation of flame retardants for thermosetting resins, such as unsaturated polyester resins, epoxy
15 resins, polyurethanes or acrylates.

1999DE119

Process for the preparation of alkylphosphonous acid
esters

Abstract

The present invention relates to a process for the preparation of alkylphosphonous acid esters which comprises

- a) reacting elemental yellow phosphorus with alkylating agents in the presence of a base to give a mixture which comprises, as principal constituents, the (metal) salts of alkylphosphonous, phosphorous and hypophosphorous acids,
- b) esterifying the principal constituents of the mixture from a) to give an ester mixture,
- c) isolating the ester of the alkylphosphonous acid from the ester mixture.

The invention likewise relates to the use of the alkylphosphonous acid esters prepared by this process as precursors for further syntheses, inter alia for the preparation of crop protection agents.

us Application 09/578,420

- 1 -

1999DE121

The invention relates to a process for the preparation of (metal) salts of alkylphosphonous acids, and to the use of the (metal) salts of alkylphosphonous acids prepared by this process.

5

Organic phosphorus compounds are increasing in industrial importance. They are employed principally for the preparation of herbicides or as herbicides themselves, as extractants and as flame retardants. The starting materials used are preferably PH_3 and phosphorus halides, which must themselves in turn be prepared from yellow phosphorus.

The reaction of red phosphorus in the superbasic medium dimethyl sulfoxide/potassium hydroxide (DMSO/KOH) with acetylenes or olefins as alkylating agent (Trofimov et al., Phosphorus, Sulfur and Silicon 55, 271, 1991) preferentially gives triorganylphosphines and triorganylphosphine oxides.

20

The alkylation of red phosphorus using acrylonitrile under the abovementioned conditions with ultrasound treatment of the reaction mixture gives predominantly secondary phosphine oxide. If 1,1-diphenylethylene is employed, tert-phosphine oxide (30%), sec-phosphine

25

- 2 -

oxide (10%) and phosphinic acid (35%) are obtained [D. Semenzin et al., Tetrahedron Letters 35, 3297, 1994].

5 It has also been attempted (Trofimov et al., Main Group Chem. News 4, 18, 1996, Phosphorus, Sulfur and Silicon, 109/110, 601, 1996) to react elemental phosphorus in its red modification with alkyl halides in the presence of potassium hydroxide, water, dioxane and a phase-
10 transfer catalyst. The main product found comprised tert-phosphine oxides (up to 75% in the case of benzyl bromide, about 60 - 65% in the case of butyl bromide). As byproducts, sec-phosphine oxides and phosphinic acid esters are obtained with 19% and 6% respectively, but
15 the former only in the presence of zinc powder as reducing agent.

However, the abovementioned processes have the disadvantage that first of all the red phosphorus or
20 organophosphorus intermediates have to be prepared. The processes are technically very complex and consequently also not economical, and the products obtained often have to be purified subsequently at great effort. In particular, the specific preparation of certain
25 compounds in high yield is frequently particularly difficult.

- 3 -

In addition, a number of starting materials, such as halogen-containing phosphorus compounds or phosphines, are unsuitable from the very beginning for a large-scale and economical process owing to their environmental toxicity.

There is therefore a demand for a process for the preparation of (metal) salts of alkylphosphonous acids which can be carried out in a simple manner and in which uniform products are obtained in high yield. A process of this type should also be clearly superior to those known hitherto in economic and environmental terms.

The invention therefore has the object of providing a process for the preparation of (metal) salts of alkylphosphonous acids which avoids the abovementioned disadvantages and with which the desired end products can be prepared without difficulty.

This object is achieved by a process of the type described at the outset, which comprises reacting elemental yellow phosphorus with alkyl halides in the presence of carbonates, bicarbonates, amides,

- 4 -

alkoxides, amine bases and/or solid hydroxides as bases.

The reaction is preferably carried out in a two-phase
5 system comprising at least one base and an organic solvent.

The alkyl halides employed are preferably methyl chloride or methyl bromide.

10

The organic solvents employed are preferably straight-
~~chain or branched alkanes,~~ alkyl-substituted aromatic
solvents, water-immiscible or only partially water-
miscible alcohols or ethers, alone or in combination
15 with one another.

The organic solvent employed is particularly preferably
toluene, alone or in combination with alcohols.

20 The reaction is preferably carried out in the presence
of a phase-transfer catalyst.

The phase-transfer catalyst is preferably a tetraalkyl-
phosphonium halide, triphenylalkylphosphonium halide or
25 tetraorganylammonium halide.

- 5 -

The temperature in the reaction is preferably from -20 to +60°C.

The temperature is particularly preferably from 0 to 5 30°C.

The reaction is preferably carried out under a pressure of from 0 to 10 bar.

10 The process according to the invention is preferably carried out by suspending or dissolving the yellow phosphorus in a solvent or solvent mixture and then reacting it with an alkyl halide and at least one base.

15 The yellow phosphorus and the alkyl halide are preferably reacted with one another in a molar ratio of from 1:1 to 1:3, where the molar ratio of yellow phosphorus to base is from 1:1 to 1:5.

20 The two-phase system obtained after the reaction is preferably separated and processed further as an aqueous phase.

The invention also relates to the use of the (metal)
25 salts of alkylphosphonous acids prepared in accordance

- 6 -
with the invention as precursors for chemical syntheses.

The invention also relates to the use of the (metal)
5 salts of alkylphosphonous acids prepared in accordance with the invention for the preparation of organo-phosphorus compounds.

The invention also relates to the use of the (metal)
10 salts of alkylphosphonous acids prepared in accordance with the invention as flame retardants or for the preparation of flame retardants.

The invention relates in particular to the use of the
15 (metal) salts of alkylphosphonous acids prepared in accordance with the invention for the preparation of flame retardants for thermoplastic polymers, such as polyethylene terephthalate, polybutylene terephthalate or polyamide.

20

The invention relates in particular to the use of the (metal) salts of alkylphosphonous acids prepared in accordance with the invention for the preparation of flame retardants for thermosetting resins, such as
25 unsaturated polyester resins, epoxy resins, polyurethanes or acrylates.

- 7 -

Surprisingly, it has been found that elemental yellow phosphorus can be reacted with alkylating agents in a two-phase system (organic solvent/base) and, if desired, in the presence of a (phase-transfer) catalyst under extremely mild conditions by the process according to the invention to give the (metal) salts of the corresponding alkylphosphonous acid $RP(:O)HOH$.

10 In addition, small amounts of dialkylphosphinic acids, trialkylphosphine oxide $R_3P(:O)$, dialkylphosphine oxide and unidentified phosphorus compounds may be formed; these can be removed from the product mixture in the usual manner. A further byproduct formed is hydrogen, 15 which can easily be separated off from the reaction mixture. The abovementioned dialkylphosphinic acids can be separated off from the reaction mixture and employed or further processed elsewhere.

20 Surprisingly, the process according to the invention gives neither phosphine (PH_3) nor alkylphosphines (RPH_2 , R_2PH) in significant amounts. Through the choice of suitable reaction conditions - such as the addition of small amounts of alcohols to the organic phase - the 25 formation of all unidentified phosphorus-containing byproducts can be minimized to a surprisingly low

- 8 -

content of a few mol% of the yellow phosphorus employed, in favor of the main product, the (metal) salts of alkylphosphonous acid.

- 5 The process according to the invention can be carried out, for example, by introducing the solvent together with the phase-transfer catalyst and warming the mixture to above the melting point of the yellow phosphorus, then adding the elemental (yellow) phosphorus, cooling the mixture to temperatures of, for example, from -10 to +30°C with vigorous stirring, and subsequently adding the alkyl halide.

15 The reaction is initiated by addition of the base. When the reaction is complete, the reaction mixture can be diluted, for example with water, and the readily volatile components (H_2 , PH_3 , RPH_2 , R_2PH and excess alkyl halide, etc.) are subsequently removed.

- 20 This process gives a base-containing/organic two-phase system whose phases are separated. The contents from the phases are determined analytically.

25 The base-containing phase can be worked up by the known methods of the prior art in order to obtain the pure

- 9 -

acids, such as, for example, alkylphosphonous acid (for example by ion exchange or distillation).

The reactants can also be combined in a different sequence, for example by introducing them continuously into a reactor (pressure tube, pressure reactor or cascade) in the above-defined molar ratio and removing them from the reactor again after a residence time of from 0.5 to 2 hours. The organic phase obtained after the phase separation, which still contains the majority of any phase-transfer catalyst employed, is advantageously recycled.

Example 1: Methylphosphonous acid

15

A solution of 26.1 g (0.05 mol) of tributylhexadecylphosphonium bromide in 1000 ml of toluene was introduced into a 5 l stainless-steel pressure reactor and pre-heated to 60°C. 31 g (1 mol) of yellow phosphorus were added, the mixture was cooled to -10°C with vigorous stirring, and 202 g (4 mol) of methyl chloride were then metered in. The mixture was then warmed to 20°C, and 500 g of 50% aqueous potassium carbonate solution were metered in over the course of 8 hours, during which the temperature was held at 20°C. Over the course of a further hour, 300 g of water were

- 10 -

added, the mixture was then stirred for a further two hours, and the reactor was subsequently decompressed via combustion. Two homogeneous liquid phases were obtained, which were separated and analyzed.

5

The aqueous phase (weight: 900 g) contained 52.7 mol% of methylphosphonous acid, 18.9 mol% of phosphorous acid, 22.7 mol% of hypophosphorous acid, 2.8 mol% of dimethylphosphinic acid in the form of their potassium salts and 2 mol% of dimethyldiphosphine.

The acids can be obtained from the salts prepared in Example 1 in a known manner, for example by ion exchange.

- 11 -

1999DE121

Patent claims

1. A process for the preparation of (metal) salts of alkylphosphonous acids, which comprises reacting
5 elemental yellow phosphorus with alkyl halides in the presence of carbonates, bicarbonates, amides, alkoxides, amine bases and/or solid hydroxides as bases.
- 10 2. A process as claimed in claim 1, wherein the reaction is carried out in a two-phase system comprising at least one base and an organic solvent.
- 15 3. A process as claimed in claim 1 or 2, wherein the alkyl halides employed are methyl chloride or methyl bromide.
- 20 4. A process as claimed in one or more of claims 1 to 3, wherein the organic solvents employed are straight-chain or branched alkanes, alkyl-substituted aromatic solvents, water-immiscible or only partially water-miscible alcohols or ethers, alone or in combination with one another.

25

- 12 -

5. A process as claimed in one or more of claims 1 to 4, wherein the organic solvent employed is toluene, alone or in combination with alcohols.
- 5 6. A process as claimed in one or more of claims 1 to 5, wherein the reaction is carried out in the presence of a phase-transfer catalyst.
- 10 7. A process as claimed in claim 6, wherein the phase-transfer catalyst is a tetraalkylphosphonium halide, triphenylalkylphosphonium halide or tetra-organylammonium halide.
- 15 8. A process as claimed in one or more of claims 1 to 7, wherein the temperature during the reaction is from -20 to +60°C.
- 20 9. A process as claimed in one or more of claims 1 to 8, wherein the temperature is from 0 to 30°C.
10. A process as claimed in one or more of claims 1 to 9, wherein the reaction is carried out at a pressure of from 0 to 10 bar.
- 25 11. A process as claimed in one or more of claims 1 to 10, wherein the yellow phosphorus is suspended or

- 13 -

dissolved in a solvent or solvent mixture and then reacted with an alkyl halide and at least one base.

5 12. A process as claimed in one or more of claims 1 to 11, wherein the yellow phosphorus and the alkyl halide are reacted in a molar ratio of from 1:1 to 1:3, where the molar ratio of yellow phosphorus to base is from 1:1 to 1:5.

10

13. A process as claimed in one or more of claims 1 to 12, wherein the two-phase system obtained after the reaction is separated and further processed.

15 14. The use of a (metal) salt of an alkylphosphonous acid prepared by a process as claimed in claims 1 to 13 as a precursor for chemical syntheses.

20 15. The use of a (metal) salt of an alkylphosphonous acid prepared by a process as claimed in claims 1 to 13 for the preparation of organophosphorus compounds.

25 16. The use of a (metal) salt of an alkylphosphonous acid prepared by a process as claimed in claims 1

- 14 -

to 13 as a flame retardant or for the preparation of flame retardants.

17. The use of a (metal) salt of an alkylphosphonous acid prepared by a process as claimed in claims 1 to 13 for the preparation of flame retardants for thermoplastic polymers, such as polyethylene terephthalate, polybutylene terephthalate or polyamide.

18. The use of a (metal) salt of an alkylphosphonous acid prepared by a process as claimed in claims 1 to 13 for the preparation of flame retardants for thermosetting resins, such as unsaturated polyester resins, epoxy resins, polyurethanes or acrylates.